



RESEARCH MEMORANDUM

PRELIMINARY INVESTIGATION OF PLATE-TYPE
MOLYBDENUM DISILICIDE FUEL ELEMENTS
FOR AN AIR-CYCLE NUCLEAR REACTOR

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SUMMARY

Molybdenum disilicide was investigated as a material for fuel elements in an air-cycle nuclear reactor. Flat, plate-type elements, 3.5 by 0.5 by 0.070 inches in size and containing 10 percent elemental natural uranium, were produced by hot pressing. The elements were acid-treated to remove surface uranium and then coated with an alumina glaze. Such an element remained stable and did not lose detectable quantities of fission fragments in a 400-hour treatment at 1800° F in a flux of 5×10^{11} neutrons per square centimeter per second.

Such elements are conveniently produced and, dependent on design and on the successful resolution of problems such as thermal shock, offer a possible method of increasing air-cycle element temperatures and related performance.

INTRODUCTION

The air cycle is particularly attractive for propulsion of nuclear-powered aircraft at the present state of the art. Present air-cycle designs are limited, however, to temperatures attainable with alloy fuel elements. Barring unexpected developments in the alloy field, higher fuel element temperatures would be possible only by means of the so-called ceramic materials. These materials include the conventional oxide ceramics, the ceramals or cermets, the carbides, and the intermetallics.

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All these materials are brittle at room temperature and any investigation of them must be based on the assumption that their high-temperature properties can outweigh any difficulties due to brittleness.

The specifications for a ceramic element would include the following properties: resistance to corrosion by air at operating temperatures, sufficient strength for operation above 2000° F, a low thermal-neutron absorption cross section, and adequate thermal conductivity. It is also essential that the elements do not lose fission fragments in operation and that they can be fabricated in forms having good heat-transfer characteristics. Resistance to thermal shock is also a requirement, although there appears to be no general agreement on specifications for this property.

Molybdenum disilicide MoSi_2 appears to meet these requirements in that it is practically unattacked by air at temperatures to 2850° F (ref. 1), its long-time, high-temperature strength is outstanding (ref. 2), and the thermal-neutron macroscopic cross section (0.063 per cm) compares well with those of alloys proposed for reactor use. The thermal conductivity (0.50 watts/cm²/°C at 200° C and decreasing with increasing temperature to 0.21 watts/cm²/°C at 600° C) appears acceptable. It is also known that molybdenum disilicide has unusual binding properties for oxides, which fact suggests that uranium oxide fuel in a molybdenum disilicide matrix would be stable.

An investigation was therefore undertaken to determine the feasibility of producing molybdenum disilicide fuel elements. The investigation was limited to simple plate-shaped elements of minimum thickness. A preliminary study (unpublished) of an aircraft air-cycle reactor based on elements of this shape from the standpoint of heat transfer and thermal stress was made in conjunction with this investigation. In the experimental investigation, particular emphasis was placed on the problem of fission-fragment loss. One of the properties of molybdenum disilicide, its resistance to common acids, was believed to offer a solution to this problem. If the elements were treated with certain acids, the surface fuel particles would be dissolved without attack on the matrix; and if the fuel were added to the elements in the form of comparatively large lumps, the surface cleaning should be more complete than if a fine-particle-size fuel were employed. The use of large-particle-size fuel would have the further advantage that fission-fragment damage within the element would be localized in areas adjacent to the fuel particles.

If the surface of the elements could be cleaned of fuel particles, the surface could be coated to further reduce fission-fragment loss. Such a coating on molybdenum disilicide would be required to serve only this purpose and would not need to protect the element against oxidation.

A flaw in the coating might result in the loss of fission fragments from the area uncovered, but no failure of the element would result. The efficiency of the cleaning and coating operations could be approximated by taking alpha-particle counts of the surfaces, as both fission fragments and alpha particles have roughly the same range (ref. 3).

Simulated fuel elements of molybdenum disilicide containing 10 percent by weight of elemental natural uranium as uranium dioxide in lumps having 60-micron average particle diameters were therefore prepared at the NACA Lewis laboratory and treated as suggested for prevention of fission-fragment loss. In-pile testing was carried out in the X-10 reactor by members of the General Electric Aircraft Nuclear Propulsion unit.

APPARATUS AND PROCEDURE

Preparation of Elements

Processes and quantities used in the preparation of elements are outlined in flow-sheet form on table I.

Powder preparation. - Natural uranium dioxide was employed throughout the investigation. The as-received sieve analysis was:

Particle size		Particles, percent by weight
Diameter, microns	Mesh	
Greater than 74	Greater than 100	Trace
Greater than 44, less than 74	Less than 100, greater than 200	10
Less than 44	Less than 200, greater than 325	29
	Less than 325	61

In order to provide an average particle size of approximately 60 microns, the 200 to 325 mesh fraction was taken. This powder was blended with molybdenum disilicide powder (average particle size, 3 microns) with a rotating blender in the quantities shown on the flow sheet to produce specimens having 10 percent contained uranium. The preparation, purification, and analysis of similar molybdenum disilicide powders are described in reference 4.

The production of a large number of elements would require a considerable quantity of the minus 200 plus 325 mesh fraction. Resintering and regrinding of the rejected sieve sizes would normally be required to produce more of this fraction. It was, however, found that if the rejected powder was mixed with a solution of synthetic starch having a dry weight of 2 percent of the weight of the powder, the mixture could be dried and the resulting hard cake ground to give another 60-micron fraction; the resintering operation was thereby avoided.

Forming. - The specimens were prepared by hot pressing in an induction-heated 6-inch-diameter graphite die having a rectangular cavity 3.5 by 0.5 inches; 15-gram charges of the powder mixture were used for 70-mil-thickness elements and 10-gram charges for 50-mil elements.

It was found possible to press two elements simultaneously by placing a thin graphite separator on the first charge and then adding the second charge. In order to facilitate removal of the thin bars, a thick wash of graphite suspended in carbon tetrachloride was applied to all graphite surfaces in contact with the charge. The pressing pressure was 1700 pounds per square inch and the heating cycle consisted in heating to a die temperature of 2950° F in 1/2 hour and holding at temperature for 1/2 hour. Power was cut off at the end of the cycle and the pressure released. The temperature was measured in a blind hole in the die approximately 1/2 inch from the specimen.

Cleaning. - Because toxicity hazards prevented grinding of the elements, the surfaces were cleaned in a two-stage process. The bars were first held overnight at 2000° F in a slowly moving air stream. This process removed most of the surface contamination due to the graphite wash. The bars were then treated in a solution of 40 percent by volume water, 40 percent nitric acid, and 20 percent hydrofluoric acid. This solution attacks molybdenum disilicide rapidly and produces a clean surface in a few minutes.

Surface uranium removal. - Uranium dioxide on the surface was removed by holding the elements in either boiling nitric acid or aqua regia for a 4-hour period; molybdenum disilicide is not attacked by either of these acids. Specimens so prepared are shown in figure 1.

Coating. - Specimens prepared as described were coated by dipping in the following slip:

Aluminum oxide, "600" mesh, g	50
Powdered commercial sodium silicate, g	50
Ball clay, g	10
Water containing 0.01 g/ml Methocel, ml	50

After dipping, the elements were dried in an oven at 170° F and then fired in air at 2560° F for 75 minutes. A coated element is shown in figure 1. The thickness of coating was between 2 and 3 mils.

Evaluations

Surface depletion evaluation. - Surface depletion of uranium was measured by alpha counting, a technique suggested by members of the

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General Electric Aircraft Nuclear Propulsion unit. Alpha counts were made on a scintillation counter for periods up to 1500 seconds. Because of the size of the instrument, only 1-square-centimeter areas could be counted at one time and it was therefore necessary to count a large number of areas on each element to be assured of the uniformity of surface conditions. The geometry of the instrument was determined from standard sources and checked against a standardized end-window Geiger counter.

High-temperature creep evaluations. - The flexure-creep test was used to approximate the creep behavior of the elements at 2200° F and above. This test consists in placing the specimen on the knife edges of a conventional high-temperature modulus-of-rupture apparatus and then applying and maintaining load for the desired stress over the desired time intervals. After removal of the specimen from the furnace, total creep was estimated by measuring the increase in length of the lower surface.

Thermal shock. - Coated and uncoated elements were quenched from a 2500° F furnace to a liquid metal (Cerrobase) bath at 900° F. Approximately one second was required for the transfer from the furnace to the bath.

In-pile testing. - A coated element was inserted in the X-10 graphite reactor at a flux of 5×10^{11} neutrons per square centimeter per second. The specimen container included a preheater for the air and thermocouples for the specimen temperature. Air was pumped over the specimen from outside the pile at a rate of 25 liters per minute and passed from the specimen to an ionization counter. For higher precision, samples of the effluent air were taken and decay curves determined. The total in-pile time was 1200 hours, of which more than 400 hours was at 1800 \pm 25° F.

RESULTS AND DISCUSSION

Comments on Preparation

The hot-pressing technique described readily produces elements 70 mils in finished thickness. Elements 50 mils thick can be produced, but a high percentage of breakage is to be expected and considerable refinement of technique would be necessary to reduce thickness much below 50 mils by the hot-pressing method.

The methods of cleaning and surface uranium removal are convenient. The efficiency of the aqua regia treatment is shown in table I by a comparison of the alpha counts between steps 3 and 4. The mechanism of this treatment is illustrated in the photomicrographs figure 2. In figure 2(a) the mixed hydrofluoric and nitric acids have attacked both the

uranium dioxide and molybdenum disilicide; however, as shown in figure 2(b), in the subsequent treatment the aqua regia has preferentially dissolved the uranium dioxide lump near the surface. The general "raisin in cake" structure of the elements is shown in these pictures.

These acid treatments are advantageous in that the uranium dissolved in these treatments should be readily recoverable. A further advantage of the nitric and hydrofluoric acid treatment is that the surface is left in an etched condition suitable for the bonding of the coating.

The particular glaze described is probably too low-firing for elements intended for use in the 2200° to 2400° F range, but suitable increases in aluminum oxide content of the slip should raise the firing point to any desired degree above the projected use temperature. A coating having a higher alumina content was found to be quite satisfactory even though the optimum firing temperature could not be attained with available equipment.

A conventional pottery glaze corrected to contain no boron, while easily applied, failed completely under moderate thermal shock conditions.

Evaluation

High-temperature creep evaluations. - Results of the flexure-creep tests can be summarized as:

Evaluation temperature, °F	Flexure stress, lb/sq in.	Time at stress, hr	Approximate elongation, percent
2400	8000	6	6.5
2400	2000	24	<.5
2200	5000	24	<.25

These limited data seem to indicate that the elements could maintain stresses in the range 1000 to 2000 pounds per square inch to 2400° F for periods of 100 hours or more. As the mechanical stresses acting on the elements would be only those from the air stream passing over them, from their own weight, and from general aircraft vibration, these strengths may be adequate.

Thermal shock behavior. - Four elements quenched as described failed. As the heat-transfer characteristics of the liquid metal were unknown, the severity of the shock cannot be estimated. The opinion has

often been expressed that the thermal shock problem can be designed out of a reactor. The extent to which thermal shock conditions occur in an aircraft reactor during shut-down and the extent to which these conditions can be minimized must be investigated before the suitability of molybdenum disilicide elements can be determined. In all the thermal shock tests, the alumina glaze remained bonded firmly to the fragments.

In-pile test. - The operators for the in-pile test reported that while the specimen was in the pile the air from the specimen at no time gave a counting rate above background (15 mr). Natural uranium even in an untreated fuel element could not be expected to give counts two or three times greater than the background; therefore, the fact that decay curves from filtered air specimens showed only the presence of the 110-minute argon isotope to be expected from irradiated air is of more significance. It was the opinion of the operators (based on other fuel-element tests) that no fission-fragment loss was occurring. Inspection of the element after removal from the pile showed little or no change in appearance of the specimen or coating.

Large correction factors are required to extrapolate the behavior of natural uranium in the X-10 reactor to that of enriched uranium in a high-flux aircraft reactor. A factor of approximately 100 can be used for enrichment correction and 160 for flux correction, a total correction of 1.6×10^4 . Because of the specification of a maximum of 10^8 fission fragments per square centimeter per second, considerable leeway still exists despite the large correction factors. Since the counts of uncoated specimen A in table I is only 2 times that of the supposedly satisfactory specimen C after furnace treatment, uncoated specimens might possibly be satisfactory.

SUMMARY OF RESULTS

1. Flat plate-type molybdenum disilicide fuel elements $3.5 \times 0.5 \times 0.070$ inches containing 10 percent elemental uranium in the form of uranium dioxide were produced by hot pressing followed by acid treatment of the surface and coating with an alumina glaze.

2. Such an as-coated element remained stable and did not lose detectable quantities of fission fragments after 400 hours at 1800°F in a flux of 5×10^{11} neutrons per square centimeter per second.

3. Such elements are conveniently produced and, dependent on the successful resolution of the design and thermal shock problems, offer one possible method of increasing air-cycle element temperatures and related performance.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, December 1, 1952

REFERENCES

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2. Maxwell, W. A.: Some Stress-Rupture and Creep Properties of Molybdenum Disilicide in the Range 1600° to 2000° F. NACA RM E52D09, 1952.
3. Goodman, Clark, ed.: The Science and Engineering of Nuclear Power. Vol. I. Addison-Wesley Press (Cambridge, Mass.) 1947, pp. 60, 281.
4. Maxwell, W. A.: Some Factors Affecting Fabrication and High-Temperature Strength of Molybdenum Disilicide. NACA RM E52B06, 1952.

TABLE I. - PREPARATION OF MoSi_2 FUEL ELEMENTS WITH CORRESPONDING
ALPHA COUNTS AT VARIOUS STAGES OF THE PROCESS

Specimens A and B prepared for testing in uncoated state;
specimen C tested in pile, coated



Preparation		Average alpha count, C, C/sq cm/sec		
		Specimens		
1. Powder preparation	<div style="display: flex; justify-content: space-around;"> <div style="text-align: center;">13.5 gm UO_2</div> <div style="text-align: center;">86.5 gm MoSi_2</div> </div> <div style="text-align: center;">↓ Blending</div>	A	B	C
2. Forming	Hot pressing	0.09	0.13	
3. Cleaning	Furnace oxidation HNO_3 -HF treatment	1.3	1.8	
4. Surface uranium removal	Aqua regia treatment	0.07	0.08	0.21
5. Coating	Dipping Drying Firing			0.008
After furnace treatment		^a 0.06		^b 0.029

^aAfter 21 hours at 2000° F.

^bAfter 90 hours at 2000° F.

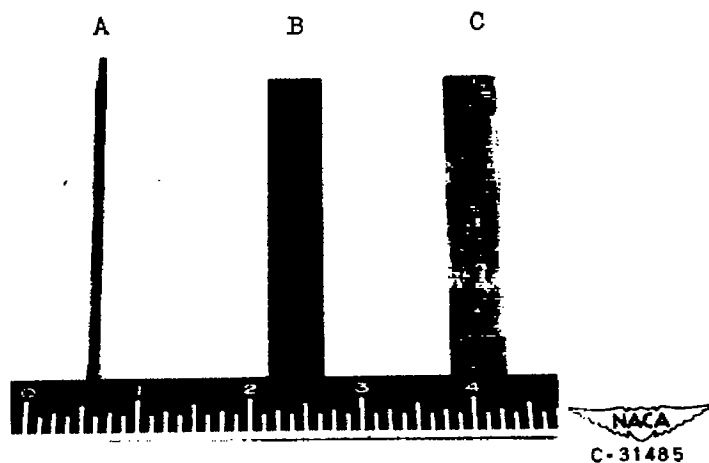
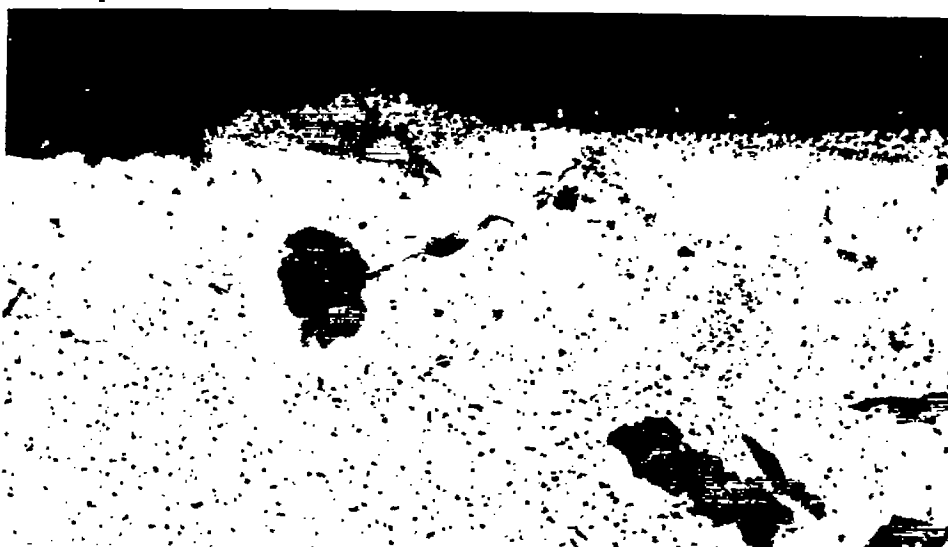


Figure 1. - Molybdenum disilicide fuel elements. A, element after aqua regia treatment; B, element similar to A after 65 hours at 2000°F ; C, element coated with alumina glaze. (scale in inches.)

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(a) Surface of MoSi_2 element after cleaning with hydrofluoric and nitric acid.



(b) Surface of figure 2(a) after aqua regia treatment.

Figure 2. - Effect of aqua regia treatment on surface uranium. Sections perpendicular to fuel element surface. Magnification, X250; unetched.



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